

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Stabilized Vinyl Alkyl Ether-maleic Anhydride Interpolymer Composition

5 We, GENERAL ANILINE & FILM CORPORATION, a Corporation organized and existing under the Laws of the State of Delaware, United States of America, of 111, West 50th Street, New York 20, County and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to stabilized vinyl alkyl ether-maleic anhydride interpolymer compositions and in particular to such interpolymers stabilized in non-aqueous systems. This invention further relates to methods for stabilizing vinyl alkyl ether-maleic anhydride interpolymers in non-aqueous and other non-reactive liquid systems and in the solid state by the addition thereto or admixture therewith of certain selected stabilizing compounds.

15 The copolymerization of vinyl alkyl ethers with maleic anhydride yields a copolymer which is more properly characterised as an interpolymer wherein both ethylenically unsaturated moieties enter into the formation of the same polymer chain. It has been indicated by infra-red spectroscopy and chemical examination and analysis that vinyl alkyl ethers and maleic anhydride interpolymerize in the molar ratio 1:1 to yield a polymer chain containing alternating maleic anhydride units and vinyl alkyl ether units. The resulting interpolymers are in general soluble in aqueous systems upon prolonged contact with water, presumably due to the hydrolysis of the anhydride groups. The interpolymers are also soluble in alkaline materials, e.g., sodium hydroxide, ammonium hydroxide, etc., again due to hydrolysis and salt formation attendant therewith, and in reactive solvents such as ethyl alcohol and the like. In non-

aqueous non-reactive materials employed as solvents such as ketones, for example, acetone and methyl ethyl ketone, ethers such as tetrahydrofuran and dioxane and halogenated aliphatic hydrocarbons such as methylene chloride and chloroform, the interpolymers are quite soluble and the anhydride configuration remains substantially unchanged. In other non-solvents which are non-reactive such as benzene, toluene and the like which are often used to prepare suspensions and slurries of such interpolymers, the anhydride groups again remain as such. This is of course quite expected. And finally, in the dry state the interpolymers which are normally solids consist essentially of anhydride moieties in the interpolymer chain. In each of the three types of environments above described, that is, solution, suspension and dry and solid states, the interpolymers are essentially, as heretofore described with the anhydride grouping, present as a true and unaffected chemical configuration. In each of these environments, however, it has been found that the interpolymers undergo substantial and serious decomposition which is manifested by a decrease in the viscosity of solutions prepared from the interpolymer material. It is often necessary to prepare specific interpolymers of specified viscosity grade and very often it is found, after suitable processing of the interpolymer, that it does not meet the expected specifications. It has further been ascertained that elevated temperatures cause a more rapid decline in the viscosity grade of the material. Since, as pointed out above, it is essential in commercial practice to obtain such interpolymers up to definite specifications of viscosity, it has become absolutely necessary to effect a stabilization of the interpolymers whereby the viscosity of the material will remain substantially unchanged under conditions which norm-

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ally lead to a decomposition and lowering of the viscosity.

It is therefore an object of this invention to provide interpolymers of vinyl alkyl ethers with maleic anhydride which are stable against degradation and/or decomposition.

It is a further object of this invention to provide vinyl alkyl ether-maleic anhydride interpolymers which are stable against degradation and/or decomposition in non-aqueous systems.

It is a still further object of this invention to provide vinyl alkyl ether-maleic anhydride interpolymers and particularly vinyl methyl ether-maleic anhydride interpolymers which are stable against degradation and/or decomposition.

It is still another object of this invention to provide vinyl alkyl ether-maleic anhydride interpolymers, and particularly vinyl methyl ether-maleic anhydride interpolymers which are stable against degradation in the solid state, in non-aqueous solvent solutions, and in non-aqueous solvent suspensions.

It is still another object of this invention to provide vinyl alkyl ether-maleic anhydride interpolymers which have uniform viscosity characteristics and are stable against degradation and decomposition in non-aqueous systems.

It is still a further object of this invention to provide vinyl alkyl ether-maleic anhydride interpolymers which are stable against degradation in non-aqueous, non-reactive solvent solutions and suspensions.

It is another object of this invention to provide processes for the preparation of stable compositions containing interpolymers of vinyl alkyl ethers with maleic anhydride, and particularly vinyl methyl ether-maleic anhydride interpolymers.

It is still another object of this invention to provide processes for the preparation of compositions containing interpolymers of vinyl alkyl ethers with maleic anhydride, and particularly vinyl methyl ether-maleic anhydride interpolymers which are stable against changes in viscosity in non-aqueous systems, and particularly when such interpolymers are present either in the solid state, in non-aqueous solvent solutions, or in non-aqueous liquid suspensions. Other objects will appear herein after as the description proceeds.

The objects of this invention are accomplished by the addition to or admixture with the vinyl alkyl ether-maleic anhydride interpolymers of small amounts of free radical inhibiting compounds. Compounds which are characterized as free radical inhibitors are well known in the art and include quinones, hydroquinones, phenols, mercaptans, aromatic amines and aromatic nitro compounds. It is indeed surprising that the addition of mere traces of such compounds in amounts of the order of from 0.00001% to 1% based on the

weight of the interpolymers would effect a substantially complete stabilization of the interpolymers with which this invention is concerned, whether the latter are present either in the solid state as a suspension or slurry in a non-aqueous liquid or in a solution in a suitable solvent. The amount of stabilizer which is preferred ranges from about 0.0001% to about 0.1% based on the weight of the interpolymers. The interpolymers which have been stabilized effectively include the general class of vinyl alkyl ether-maleic anhydride interpolymers, and particularly those wherein vinyl alkyl ethers have as the alkyl moiety, alkyl groups of from 1 to 8 carbon atoms. These include as the vinyl alkyl ether:—

vinyl methyl ether

vinyl ethyl ether

vinyl n-propyl ether

vinyl isopropyl ether

vinyl n-butyl ether

vinyl isobutyl ether

vinyl amyl ether

vinyl isohexyl ether

vinyl n-heptyl ether

vinyl iso-octyl ether

vinyl n-octyl ether

The following examples will serve to illustrate the present invention without being deemed limitative thereof. Parts are by weight unless otherwise indicated.

#### EXAMPLE 1

An interpolymers of methylvinyl ether and maleic anhydride is prepared as follows:—

Into a 2-liter autoclave there are charged at room temperature:—

1000 g. methyl vinyl ether;

200 g. powdered maleic anhydride; and

10 g. lauroyl peroxide.

The autoclave is purged three times with air to a pressure of 25 pounds and then adjusted to 9-1/2 pounds. The mixture is then slowly heated to 55° C. over a period of 16 minutes. The temperature then rises due to the heat of the reaction to 89° C. and the internal pressure to 245 pounds. The reaction mixture is then cooled to room temperature over a period of 40 minutes. Excess methyl vinyl ether is removed and the product stirred under vacuum for one hour. The product is then discharged and dried at 34° C. in vacuo for 12 hours. Yield, 320 grams of interpolymers. The reduced viscosity of 1.0% solution in methyl ethyl ketone is 3.45.

#### EXAMPLE 2

A slurry of the interpolymers of Example 1 is prepared in benzene (non-solvent for the interpolymers) containing 15% solids. A similar slurry is also prepared containing in addition 0.1% of phenyl- $\alpha$ -naphthylamine. Both samples are placed in an oven for 18 hours at 50° C. The samples are then removed from the oven and the solid recovered

from the slurry by filtration and dried for 20 minutes in a Cenco infra-red drier. Reduced viscosity measurements of 1% solution in methyl ethyl ketone are then made. The amine stabilized product is found to have a reduced viscosity of 3.48 whereas the interpolymer containing no stabilizer has a reduced viscosity of 2.94. The original interpolymer as described in Example 1 has a reduced viscosity of 3.45. It is clear that the addition of 0.1% of a selected amine has effected an outstanding stabilization of the interpolymer under the conditions recited.

#### EXAMPLE 3

Example 2 is repeated except that the samples are subjected to a temperature of 60° C. for 24 hours. The stabilized sample shows no change in viscosity characteristics when measured as in Example 2 whereas the unstabilized product suffers a 10% decline in viscosity.

#### EXAMPLE 4

Example 3 is repeated employing, however, in lieu of 0.1% amine, the following concentrations:—

0.02%  
0.004%

The interpolymer stabilized with 0.02% not only does not suffer any loss in viscosity characteristics but actually is found to have increased in viscosity about 1%. The interpolymer containing smaller amount of stabilizer shows very little decrease in viscosity amounting to about 3%.

#### EXAMPLE 5

The procedure of Example 2 is repeated employing, however, tertiary butyl catechol. The slurries are subjected to a temperature of 85° C. for 24 hours. With 0.1% stabilizer there is substantially no change in the viscosity characteristics of the interpolymer. The unstabilized material suffers a loss of about 40% in viscosity characteristics. Using smaller amounts of stabilizer, that is, 0.02% and 0.004%, yields interpolymers of substantially the same degree of stabilization and viscosity characteristics as the product containing 0.1% stabilizer.

#### EXAMPLE 6

Example 3 is repeated employing the following stabilizers:—

- a) tertiary-dodecyl mercaptan
- b) 2,4,6-trinitrotoluene
- c) 2,4,6-tritertiary-butyl phenol
- d) chloranil
- e) nitrodimethylaniline
- f) tetrahydroxyleucoanthraquinone
- g) benzoquinone
- h) hydroquinone

Excellent stabilization is effected in each instance.

#### EXAMPLE 7

Example 6 is repeated employing, however, concentration of 0.02% and 0.004% in lieu of 0.1%. Outstanding improvements are obtained.

#### EXAMPLE 8

Ten parts of the dry interpolymer of Example 1 is placed in an oven at 90° C. for 48 hours. The reduced viscosity of 1% solution in methyl ethyl ketone is found to be 2.60 as compared with the original 3.45. To another ten part sample there is added and thoroughly admixed therewith, 0.1% phenyl  $\alpha$ -naphthylamine, and after 48 hours at 90° C., the viscosity is found to be 3.42.

#### EXAMPLE 9

Example 8 is repeated except that the ten parts of interpolymer are dissolved in 90 parts of dioxane in each instance. The unstabilized solution undergoes a severe viscosity drop whereas the stabilized solution remains substantially unchanged in viscosity.

#### EXAMPLE 10

Example 1 is repeated employing in lieu of methyl vinyl ether, an equivalent amount of ethyl vinyl ether. The resulting interpolymer has a reduced viscosity of 3.75.

#### EXAMPLES 11—14

Example 1 is again repeated employing:—  
Example 11 vinyl n-butyl ether  
Example 12 vinyl isobutyl ether  
Example 13 vinyl n-heptyl ether  
Example 14 vinyl iso-octyl ether  
in equivalent amounts for the vinyl methyl ether of Example 1.

#### EXAMPLE 15

The products of Examples 10—14 in the solid state are effectively stabilized with 0.1% phenyl  $\alpha$ -naphthylamine when subjected to the conditions set forth in Example 2. In the absence of the stabilizer, there is a marked decrease in the viscosity characteristics of the interpolymers.

In the following examples the outstanding stabilizing effect of such small amounts as but a few parts per million is demonstrated.

#### EXAMPLE 16

An interpolymer of vinyl methyl ether and maleic anhydride is prepared as in Example 1. This particular interpolymer is characterized as having a specific viscosity of 2.07. A slurry of this material is prepared in benzene containing 20% solids. A similar slurry is prepared to which there is added 5 parts per million on a solids basis of tertiary butyl catechol. Both slurries are then heated in a vacuum oven at 140° C. for 2 hours. The unstabilized product has a specific viscosity in methyl ethyl ketone of 1.75. This is a loss of about 16%. The stabilized material

shows a specific viscosity of 1.99, which is a loss of only about 4%.

#### EXAMPLE 17

- 5 The procedure of Example 16 is repeated except that the slurries are heated for 4 hours at 140° C. The unstabilized slurry exhibits a loss of only 6%.

#### EXAMPLE 18

- 10 Example 16 is once again repeated except that the slurries are heated for 6 hours at 140° C. The unstabilized product shows a viscosity loss of 31% whereas the stabilized material undergoes a loss of only about 13%.

#### EXAMPLE 19

- 15 Example 16 is again repeated employing, however, only 1 part per million of tertiary butyl catechol based upon the interpolymers solids. The unstabilized product undergoes a viscosity loss of over 20% whereas the stabilized material exhibits a loss of less than 5%.

#### EXAMPLE 20

- 20 Examples 16 and 19 are again repeated employing the various stabilizers used in Example 6. In each instance there is a tremendous improvement in stabilization even at the extremely low stabilizer concentrations employed.

#### EXAMPLE 21

- 30 Examples 16, 19 and 20 are again repeated employing, however, as the interpolymers a vinyl butyl ether maleic anhydride interpolymers as prepared in Example 11.

#### EXAMPLE 22

- 35 Example 21 is repeated employing the interpolymers described in Examples 12, 13 and 14.

#### WHAT WE CLAIM IS:—

- 40 1. A non-aqueous stabilized composition of matter comprising an interpolymers of vinyl alkyl ether with maleic anhydride and a stabilizing amount of a free radical inhibitor.
- 45 2. A non-aqueous stabilized composition of matter comprising an interpolymers of vinyl methyl ether with maleic anhydride and a stabilizing amount of a free radical inhibitor.
- 50 3. A non-aqueous stabilized composition of matter comprising an interpolymers of vinyl alkyl ether with maleic anhydride and from 0.00001% to 1% based on the weight of said interpolymers of a free radical inhibitor.
- 55 4. A non-aqueous stabilized composition of matter comprising an interpolymers of vinyl ether with maleic anhydride and from 0.00001% to 1% based on the weight of said interpolymers of a free radical inhibitor.
- 60 5. A non-aqueous stabilized composition of matter comprising an interpolymers of vinyl ethyl ether with maleic anhydride and from 0.00001% to 1% based on the weight of said interpolymers of a free radical inhibitor.

6. A non-aqueous stabilized composition of matter comprising an interpolymers of vinyl iso-propyl ether with maleic anhydride and from 0.00001% to 1% based on the weight of said interpolymers of a free radical inhibitor.

7. A non-aqueous stabilized composition of matter comprising an interpolymers of vinyl iso-butyl ether with maleic anhydride and from 0.00001% to 1% based on the weight of said interpolymers of a free radical inhibitor.

8. A non-aqueous stabilized composition of matter comprising an interpolymers of vinyl alkyl ether with maleic anhydride and a stabilizing amount of a free radical inhibitor selected from the class consisting of quinones, hydroquinones, phenols, mercaptans, aromatic amines and aromatic nitro compounds.

9. A non-aqueous stabilized composition of matter comprising an interpolymers of vinyl alkyl ether with maleic anhydride and from 0.00001% to 1% based on the weight of said interpolymers of a free radical inhibitor selected from the class consisting of quinones, hydroquinones, phenols, mercaptans, aromatic amines and aromatic nitro compounds.

10. A non-aqueous stabilized composition of matter comprising an interpolymers of vinyl methyl ether with maleic anhydride and from 0.00001% to 1% based on the weight of said interpolymers of a free radical inhibitor selected from the class consisting of quinones, hydroquinones, phenols, mercaptans, aromatic amines and aromatic nitro compounds.

11. A composition as defined in Claim 10 wherein the amine is a polycyclic, carbocyclic amine.

12. A composition as defined in Claim 11 wherein the amine is phenyl  $\alpha$ -naphthylamine.

13. A composition as defined in Claim 10 wherein the phenol is tertiary-butyl catechol.

14. In a method for the preparation of a viscosity-stable composition obtained from the interpolymers of a vinyl alkyl ether with maleic anhydride in the presence of a peroxide catalyst, the improvement which comprises adding to the isolated interpolymers a stabilizing amount of a free radical inhibitor.

15. In a method for the preparation of a viscosity-stable composition obtained from the interpolymers of a vinyl methyl ether with maleic anhydride in the presence of a peroxide catalyst, the improvement which comprises adding to the isolated interpolymers from 0.00001% to 1% based on the weight of said interpolymers of a free radical inhibitor.

16. The stabilized composition of matter substantially as described.

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